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COMPLETE SPECIFICATION

Esters of Styrene-Maleic Anhydride Copolymers, their production and use

We, MOBIL OIL CORPORATION, a corporation organised under the laws of the State of New York, United States of America, of 150 East 42nd Street, New York, New York 10017, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to esters of styrene-maleic anhydride copolymers and to liquid hydrocarbon compositions containing them and to a method of preparation of the esters.

Various materials have been proposed in the past as fluidity improvers in liquid hydrocarbons. For example U.S. Patent No. 2,977,334 describes the use of certain ethylene/maleic anhydride copolymer derivatives as pour point modifiers. The derivatives are, however, difficult to prepare from the copolymers. The process involves conversion of a half-ester or half-amide, followed by reaction of the remaining carboxyl or anhydride groups or of the ester or amide groups. Obviously, this requires a considerable expenditure of time and money.

U.S. Patent No. 2,978,395 describes the use of styrene/unsaturated ester copolymers as pour point depressants. These copolymers are produced by exposing the reactants to radiation. This method is not very attractive because of limited radiochemical conversions and the general industrial preference for chemical polymerisation methods.

These, and various other additives too, have also been unsatisfactory when the hydrocarbons to be treated boil over a substantially wide range. Furthermore, some fluidity improvers have proved effective in certain types of oil, while exhibiting more limited improvement in other types. More specifically, it would be very desirable to employ a fluidity improver in liquid hydrocarbons which boil,

for example, within the range 75° to 1000°F. and which are also effective in various types of oils such as crude or petroleum residual oils.

We have now discovered a class of materials which are extremely effective as pour point depressants and which can be easily prepared.

These materials are the esters of styrene-maleic anhydride copolymers which contain more than 20 carbon atoms in the alkyl portion. They are used in relatively small amounts in the hydrocarbon compositions and yet produce a satisfactory improvement in fluidity.

In accordance with the invention, these esters can be effectively employed in the liquid hydrocarbon compositions as pour point depressants and fluidity improvers in an amount from about .001 per cent to about 1 per cent, and preferably from about .01 per cent to about 0.5 per cent, by weight, of the total weight of the liquid hydrocarbon composition. Preferred esters are those which have from 20 to 24 carbon atoms in the alkyl portion.

The esters are produced by copolymerizing styrene and maleic anhydride and then esterifying the resultant copolymer with a saturated aliphatic alcohol having at least 20 carbon atoms in the molecule.

The liquid hydrocarbons improved in accordance with the present invention may comprise any hydrocarbons in which fluidity improvement is desirable. A field of specific applicability, in accordance with the present invention, is in the improvement of liquid hydrocarbons boiling at a temperature from about 75°F. to about 1000°F. Of particular importance is the treatment of petroleum distillate oils which have pour and flow points above 75°F. and which boil as high as 750°F. or even higher. It should be noted, in this respect, that the term "distillate oils" is not intended to be restricted to straight-run distillate fractions. The distillate oils can be straight-run distillate, catalytically or therm-

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ally cracked (including hydrocracked distillate oils) or mixtures of straight-run distillate oils and naphthas, with cracked distillate stocks. Moreover, such oils can be treated in accordance with well known commercial methods, such as acid or caustic treatment, hydrogenation, solvent refining and clay treatment.

The distillate oils are characterized by their relatively low viscosity and pour point. The principal property which characterizes these hydrocarbons, however, is their distillation range. As hereinbefore indicated, this range will preferably lie between about 75°F. and about 750°F. Obviously, the distillation range of each individual oil will cover a narrower boiling range falling, nevertheless, within the above mentioned limits. Likewise, each oil will boil substantially and continuously throughout its distillation range.

As hereinbefore indicated, the liquid hydrocarbon compositions improved in fluidity characteristics through the use of the ester copolymers of the present invention have broad applicability to liquid hydrocarbon compositions in the form of crude oils or petroleum residual oils. Thus, the fluidity characteristics of very high wax-containing petroleum residual oils, such as the residuum or North African crude oils designated as Zelen, or similar petroleum oils which boil above 650°F. and have pour points above 75°F. have broad applicability. Another specific type of crude oil to which the present invention also has broad applicability is the Amal crudes.

As previously described, the novel fluidity improvers of the present invention comprise esters of styrene maleic anhydride copolymers having at least 20 carbon atoms in the alkyl portion. In general, the polymerization reaction for producing the above-described copolymers is carried out at a temperature from about 50°C to about 250°C, and preferably from about 100°C to about 200°C, in the presence of an organic peroxide catalyst, for example, benzoyl peroxide or ditertiary butyl peroxide, in an amount sufficient to permit polymerization to take place. Small amounts of the catalyst are usually sufficient for such purpose, for example, amounts from about 0.1 percent to about 10 per cent, by weight, of the polymerization mixture. In preparing the ester copolymer, 1 mole of styrene and 1 mole of maleic anhydride are subjected to copolymerization. Thereafter, to the reaction mixture are added 1 or 2 moles of a saturated straight-chain alcohol having a minimum of 20 carbon atoms, which in the presence of an acid catalyst will result in esterification of the copolymer.

The following data and examples will serve to illustrate the preparation of the novel ester copolymers of the present invention and their efficacy for improving the fluidity characteristics of liquid hydrocarbon compositions.

EXAMPLE 1

Preparation of dibehenyl (didocosanyl) ester of styrene maleic anhydride copolymer.

26 grams (0.25 mole) of styrene, 24.5 grams (0.25 mole) maleic anhydride, 0.5 gram of benzoyl peroxide and 200 grams of xylene as a diluent were stirred to a temperature of about 135°C over a period of four hours. 165 grams (0.5 mole) of commercial grade behenyl alcohol and 7 grams of paratoluene sulfonic acid were then added to the reaction mixture, and the resulting mixture was stirred with refluxing to a temperature of about 200°C. The resulting product was found to comprise a dibehenyl (didocosanyl) ester of styrene maleic anhydride copolymer.

EXAMPLE 2

Preparation of dieicosanyl ester of styrene maleic anhydride copolymer.

26 grams (0.25 mole) of styrene, 24.5 grams (0.25 mole) of maleic anhydride, 0.5 gram of benzoyl peroxide and 200 grams of xylene as a diluent were stirred to a temperature of about 115°C over a period of about four hours. 150 grams (0.5 mole) of commercial grade 1-eicosanol and 6 grams of paratoluene sulfonic acid were added to the reaction mixture, and the resulting mixture was stirred with refluxing to a temperature of about 220°C. The resulting product was found to comprise a dieicosanyl ester of styrene maleic anhydride copolymer.

EXAMPLE 3

Preparation of ditetracosanyl ester of styrene maleic anhydride copolymer.

13 grams (0.125 mole) of styrene, 12.25 grams (0.125 mole) of maleic anhydride, 0.25 gram of benzoyl peroxide and 100 grams of xylene as a diluent were stirred to a temperature of about 100°C over a period of about two hours. 88 grams (0.25 mole) of commercial grade 1-tetracosanol and 5 grams of paratoluene sulfonic acid were added to the resulting reaction mixture and stirred with refluxing to a temperature of about 215°C. The resulting product was found to comprise a ditetracosanyl ester of styrene maleic anhydride copolymer.

EXAMPLE 4

Preparation of monobehenyl ester of styrene maleic anhydride copolymer.

26 grams (0.25 mole) of styrene, 24.5 grams (0.25 mole) of maleic anhydride, 0.5 gram of benzoyl peroxide and 200 grams of toluene as a diluent were stirred to a temperature of about 100°C over a period of about three hours. 83 grams (0.25 mole) of commercial grade behenyl alcohol and 5 grams of paratoluene sulfonic acid were added to the resulting reaction mixture and stirred with refluxing to a temperature of about 205°C. The resulting product was found to comprise a monobehenyl ester of styrene maleic anhydride copolymer.

The individual ester copolymers produced

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in accordance with the foregoing examples 1 to 4 were next blended into an Amal crude oil and subjected to a series of tests for determining their efficacy as fluidity improvers. The Amal crude oil comprised a highly paraffinic, waxy, low sulfur, high asphaltene content crude oil from Libya in Africa. The same tests were also applied with respect to an Amal residual fuel oil for determining the efficacy of the present ester copolymers as fluidity improvers.

The ester copolymers of examples 1 to 4, as hereinbefore described and having a minimum of 20 carbon atoms in the respective alkyl portions, were subjected to test method ASTM Test No. D-97 for determination of respective pour points. This test was applied against the uninhibited as well as against samples of the same oil containing the indicated concentrations of the respective ester copolymers produced in accordance with the foregoing examples 1 to 4. The results obtained are shown in the following Table I.

TABLE I
ASTM Pour Test Results
(ASTM Test No. D-97)

	Conc., % Wt.	Pour Point, °F.
Uninhibited crude oil	0.	65
" " " +Example 1	0.06	30
" " " +Example 2	0.06	35
Uninhibited crude oil	0.	70
" " " +Example 3	0.06	25
" " " +Example 4	0.10	35
Uninhibited residual oil	0.	100
" " " +Example 1	0.10	65
" " " +Example 2	0.10	85
" " " +Example 3	0.10	75
" " " +Example 4	0.50	80

It will be apparent from the data set forth in the foregoing Table I that the ester copolymers of the present invention are highly effective as fluidity improvers in liquid hydrocarbons. As will be understood, results will vary with respect to the specific ester copolymers employed. In order to accomplish any given improvement, many of the aforementioned ester copolymers can be employed in very small amounts. Others can be effectively employed at the aforementioned practical concentrations of from about .01 to about 0.5 per cent, by weight, of the liquid hydrocarbon composition.

For purposes of comparison in demonstrating the aforementioned criticality of the chain length of the ester employed for the preparation of the ester copolymers of the present invention which contain at least 20 carbon atoms in the alkyl portion, the di-1-octadecyl ester of styrene maleic anhydride copolymer was individually blended in individual samples of the aforementioned Amal crude and residual oils, and also subjected to the aforementioned ASTM D-97 pour test and compared against the uninhibited oil. It was found that no significant improvement in pour point was realized. From the foregoing, it will be apparent that no significant improvement in fluidity characteristics as demonstrated by the respective pour point data is achieved by employing ester styrene maleic anhydride copolymers which contain less than 20 carbon atoms in the respective alkyl portions.

To further demonstrate the efficacy of the novel ester copolymers of the present invention as fluidity improvers in liquid hydro-

carbons, the individual ester copolymers were next blended into an Amal crude oil of the type hereinbefore described, and subjected to a series of tests for determination of fluidity characteristics by an evaluation of constant shear rates (94 secs.⁻¹) at 40°F. This test involves the use of a Ferranti-Shirley viscometer in which the cone is set on a plate sufficiently close to make electrical contact. The cone is rotated at a preset speed of 5 R.P.M., and the torque required to maintain this speed is recorded as a function of time. This test was applied against the uninhibited as well as against samples of the same oil containing the indicated concentrations of the respective ester copolymers produced in accordance with the foregoing examples 1 to 4. The results obtained are shown in the following Table II.

TABLE II

Constant Shear Rate (94 secs.⁻¹) Test

Evaluation at 40°F. of Additives Blended in Amal Crude Oil

Additive	Conc. % Wt.	Peak Shear Stress (Dynes/cm ²)	Viscosity After 100 Sec Shear (Poise)
Uninhibited crude oil	0.00	2550	9.1
" " " + Ex. 1	0.06	612	3.2
" " "	0.00	3050	8.3
" " " + Ex. 2	0.06	758	4.4
Uninhibited cured oil	0.00	3480	8.3
" " " + Ex. 3	0.06	663	4.5
" " " + Ex. 4	0.06	1823	7.7

It will be apparent from the data set forth in the foregoing Table II that the ester copolymers of the present invention are highly effective as fluidity improvers in liquid hydrocarbons on the basis of constant shear rate evaluations.

For purposes of comparison in demonstrating the aforementioned criticality of the chain length of the ester employed for the preparation of the ester copolymers of the present invention which contain at least 20 carbon atoms in the alkyl portion, the di-1-octadecyl ester of styrene maleic anhydride copolymer was individually blended in another sample of the aforementioned Amal crude oil, and also subjected to the aforementioned constant shear rate test and compared against the uninhibited oil. It was found that no significant improvement in fluidity characteristics was realized. From the foregoing it will be apparent that no significant improvement in fluidity characteristics as demonstrated by the respective constant shear rate evaluations is achieved by employing ester styrene maleic anhydride copolymers which contain less than 20 carbon atoms in the respective alkyl portions.

WHAT WE CLAIM IS:—

1. An ester of a styrene maleic anhydride copolymer which contains at least 20 carbon atoms in the alkyl portion.
2. An ester according to claim 1 in which the alkyl portion of the ester contains from 20 to 24 carbon atoms.
3. An ester according to claim 1 in which the alkyl portion of the ester is a dilauryl, monodocosanyl, didocosanyl or ditetracosanyl group.
4. An ester substantially as herein described with reference to any of the Examples.
5. A method of making an ester of a styrene maleic anhydride copolymer, which comprises copolymerizing styrene and maleic anhydride and then esterifying the copolymer with a saturated aliphatic alcohol containing at least 20 carbon atoms.
6. A method according to claim 5 in which the alcohol contains from 20 to 24 carbon atoms.
7. A method according to claim 5 or 6 in which the polymerization is carried out at a temperature of from 50° to 250°C.
8. A method of making an ester of a styrene maleic anhydride copolymer, substan-

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fully as herein described with reference to any of the examples.

- 5 9. A liquid hydrocarbon composition which comprises a liquid hydrocarbon and an ester of a styrene maleic anhydride copolymer containing at least 20 carbon atoms in the alkyl portion.

- 10 10. A composition according to claim 9 which contains from 0.001 to 1 percent by weight of the ester.

11. A composition according to claim 10 which contains from 0.01 to 0.5 percent by weight of the ester.

- 15 12. A composition according to any of claims 9 to 11 in which the alkyl portion of the ester contains from 20 to 24 carbon atoms.

13. A composition according to any of

claims 9 to 12 in which the liquid hydrocarbon has a boiling range from 75° to 1000°F.

- 20 14. A composition according to any of claims 9 to 13 in which the liquid hydrocarbon is a crude oil or a petroleum residual oil.

- 25 15. A liquid hydrocarbon composition according to any of claims 9 to 14 containing a copolymer produced substantially as herein described with reference to any of the Examples.

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